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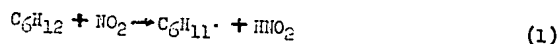
THE MECHANISM OF OXIDATION AND NITRATION OF CYCLOHEXANE
WITH NITRIC ACID AND OXIDES OF NITROGEN. I

A. I. Titov and M. K. Matveyeva

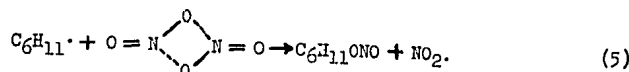
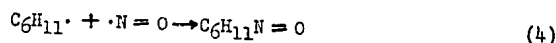
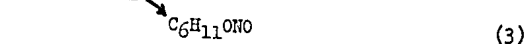
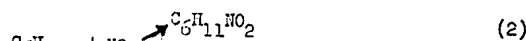
[Note: The experimental part has been omitted.]

The oxidation and nitration of cyclohexane with nitric acid has been investigated earlier by Markovnikov [1], Nametkin [2], and Aschan [3]. S. S. Nametkin studied this reaction most circumstantially from the standpoint of classical organic chemistry.

The theory of nitrating the paraffinic chain which we developed permitted us to find a mechanism for this reaction and discover new directions in which it proceeds [1]. According to our theory, the initial, elementary stage in the oxidation and nitration of cyclohexane with nitric acid as well as with oxides of nitrogen is the genesis of free cyclohexyl after an effective collision of the hydrocarbon with a radical-like monomer of nitrogen dioxide:



The main further conversions of cyclohexane in the sphere of nitration will be reactions 2-5:



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When nitration takes place in the liquid phase at elevated temperatures, the role of reactions 4 and 5 will be slight except in special cases, and hence, the principal primary products of the reaction will be nitrocyclohexane and cyclohexylnitrite. Nitrocyclohexane must remain preserved in the end products of the reaction, but cyclohexylnitrite, through an intermediate formation of cyclohexanol, must convert to a mixture of adipic acid and lower dicarboxylic acids.

According to our theory, nitric acid does not cause an independent oxidizing and nitrating action. Nitric acid has an influence on the reaction velocity and the relationship between the principal directions of the reaction because of its participation in the equilibrium $2\text{HNO}_3 + \text{NO} \rightleftharpoons 3\text{NO}_2 + \text{H}_2\text{O}$, where it serves as a source and medium for the progressive regeneration of nitrogen dioxide from the lower oxides. At high temperatures, pyrolysis products of nitric acid such as nitric acid anhydride, NO_3 , HO_2 , etc., could become active. Experiments confirmed these conclusions based on the general theory on the nitration of the paraffinic chain. First, we showed that cyclohexane will react noticeably with nitrogen dioxide even at ordinary temperatures and that this reaction will be relatively fast at 100° . Under appropriate conditions this reaction led principally to the formation of adipic acid and nitrocyclohexane, i. e., the same products as in the reaction of cyclohexane with nitric acid.

Then, by carrying out the reaction with nitric acid under the same conditions as with nitrogen dioxide, and also according to S. S. Mametkin's method, we proved that the interaction practically does not occur in the absence of nitrogen dioxide in the sphere of the reaction, and that the extent of its occurrence is proportional to the addition of NO_2 . Moreover, when oxidation with nitrogen dioxide takes place under appropriate conditions, addition of nitric acid has a negative effect on the yield of the reaction because of the presence of water in the acid and a shift to the right in the equilibrium $3\text{NO}_2 + \text{H}_2\text{O} \rightleftharpoons 2\text{HNO}_3 + \text{NO}$.

That the reaction takes place in the gaseous phase through the interaction of cyclohexane with nitrogen dioxide is proved by the fact that the reaction occurs in sealed tubes at 100° upon heating of a mixture of the hydrocarbon with nitrogen dioxide in quantities that ensure complete evaporation. The absence of any oxidizing or nitrating action of nitric acid under these conditions follows from the results of the nitration according to Mametkin with addition of ammonium sulfate, where the reaction could have taken place in the gaseous phase, since the tubes were filled to no more than one third of their volume.

Experimental proof of the absence of a reaction between nitric acid and the hydrocarbon at high temperatures ($> 200^\circ$) is extremely difficult because of spontaneous decomposition of nitric acid and the formation of nitrogen dioxide. Furthermore, it cannot be denied that at sufficiently high temperatures direct interaction of nitric acid with the hydrocarbon may become noticeable. It is even more probable that there will be reactions with the pyrolysis products of HNO_3 , namely, H-O_2 , HO_2 , NO_2 , etc. All experiments carried out at $320-340^\circ$ indicated that the yield of reaction product resulting from the interaction between cyclohexane and nitrogen dioxide was almost 10 times greater than that in analogous experiments with nitric acid of sp gr 1.4. By increasing the length of time during which the nitric acid remained in the reaction tube, the yield of the reaction product was somewhat increased. This is explained by an increase in the possibility of the decomposition of nitric acid. These results at least indicate the low rate of the reaction with nitric acid even at very high temperatures.

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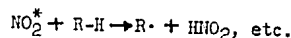
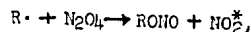
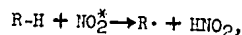
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That the primary reaction of cyclohexane with nitrogen dioxide (1) must be of the radical type is confirmed by a series of experimental data. This conclusion is supported by the fact that the reaction takes place in the gaseous phase. The facts that there is practically no change in the yield of the reaction when the amount of nitric acid is increased and that there is a great increase in the yield when the amount of cyclohexane is increased indicate that the reaction takes place in the hydrocarbon phase, which also agrees with the assumed radical character of the reaction. The lack of any noticeable acceleration in the reaction between nitrogen dioxide and cyclohexane when strong protonic and aprotic acids (i. e., sulfuric acid, aluminum trichloride, titanium tetrachloride, and iodine) are added, indicates the small role of the ionic character of the reaction in the primary stage of the oxidation and nitration of the paraffinic chain.

The above-stated points, although characteristic for the nitration of cyclohexane, are entirely different from those which apply to the simplest aromatic compound, i. e., benzene, a substance which is related to cyclohexane. This corresponds to general differences in the nitration of saturated hydrocarbons as compared with aromatic hydrocarbons and the accepted mechanisms of these nitrations [5]. In agreement with the above condition, we also found that additions of mercury salts have no noticeable effect on the nitration of cyclohexane.

In agreement with the accepted mechanism, the reaction of the nitration and oxidation of cyclohexane does not possess a chain character. This conclusion was confirmed by a lack of difference in the velocity of the reaction when a mixture of cyclohexane and nitrogen dioxide was passed through an empty tube in one experiment, as compared with another experiment in which the mixture was passed through a tube filled with broken glass. However, at a high concentration of nitrogen dioxide there is apparently a possibility for the development of long chains by this type of scheme.



Rupture of the chains will occur at the expense of the coupling of radicals with NO and NO₂, while branching will occur at the expense of side reactions of oxidation of cyclohexylnitrite and cyclohexanol. It is probable that such a case was realized in one of our experiments when 0.84 g of cyclohexane and 4.5 g of nitrogen dioxide were heated in a sealed tube to 100°. The tube exploded with a great demolishing effect.

SUMMARY

On the basis of experimental results obtained by comparing, under various conditions, the behavior of cyclohexane toward nitrogen dioxide with its behavior towards nitric acid, the following conclusions can be drawn:

1. The reaction between cyclohexane and nitrogen dioxide is comparatively rapid and yields the same products as the nitration with nitric acid according to the Konovalov-Nametkin method.
2. The oxidation and nitration of cyclohexane with nitric acid take place through an intermediate reaction with nitrogen dioxide.

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3. That the primary stage of the reaction must be of the radical type is confirmed by the fact that it takes place in the gaseous and hydrocarbon phases, by the lack of any accelerating action due to strong protonic and aprotic acids, and also by the lack of any effect due to the addition of mercury salts.

4. The general theory for the nitration of the paraffinic chain, developed earlier, is applicable to the oxidation and nitration of cyclohexane.

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